
Contaminant Hydrogeology

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6.7.3 Sulfur

Sulfur is released to the environment by the weathering of minerals containing the element. Rock containing pyrite can be oxidized to release sulfur, with microorganisms acting as a catalyst and mediating the oxidation. This is the source of the acidic water that drains from many areas that have been mined. Sulfuric acid is widely used in industrial processes. Sulfur can be released to the environment by the processing of sulfide ores and by the burning of fossil fuels, all of which contain sulfur to some degree.

Sulfur can exist in valence states ranging from S^{-2} to S^{+6} . Figure 6.8 is an Eh-pH diagram showing the stability of the two oxidized forms of sulfur, HSO_4^- and SO_4^{2-} , and the three reduced forms, S^{2-} , HS^- , and H_2S (aqueous). The field of stability for elemental sulfur is also shown. The total sulfur activity used in computing the diagram is 10^{-3} mol/L or 96 mg/L as SO_4^{2-} . If a greater total sulfur activity were used, the stability field for elemental sulfur would be larger. Although this is a very useful diagram for understanding the equilibrium conditions for dissolved sulfur, the redox reactions can be slow if microbes are not mediating the reactions. Hence, it may take a long time for the system to reach equilibrium.

Gypsum (calcium sulfate) is quite soluble in water ($K_{eq} = 10^{-4.6}$) and, except for waters with extremely high sulfate, would not be a sink for sulfate. Strontium sulfate is sparingly soluble ($K_{eq} = 10^{-6.5}$), whereas barium sulfate is nearly insoluble ($K_{eq} = 10^{-10.0}$). However, strontium and barium are not found in much abundance in natural waters. Sulfate could act as a sink for strontium and barium.

6.7.4 Nitrogen

Nitrogen is another element that can occur in both oxidized and reduced forms as well as the elemental state. The common forms of inorganic nitrogen include nitrate, NO_3^- , nitrite, NO_2^- , nitrogen gas, N_2 , ammonium, NH_4^+ and cyanide, CN^- . Nitrogen is also a major constituent of organic matter in the form of amino acids. The majority (78%) of the Earth's atmosphere is nitrogen gas. Atmospheric nitrogen can be "fixed", or converted to nitrate, by cyanobacteria in lakes and the ocean and by bacteria living on the roots of plants such as legumes and lichens. Atmospheric nitrogen can also be converted to oxidized and reduced forms via fertilizer production and by heating it to high temperatures in internal combustion engines, power plants, lightning discharges and forest fires. Rainwater contains dissolved nitrate and ammonia. Nitrogen is released to the subsurface from sewage, animal wastes, and fertilizers.

In soil and ground water, oxidation and reduction of nitrogen species is accomplished by microorganisms. Under oxidizing conditions ammonia is converted to nitrite, which is converted to nitrate. Nitrite is a very reactive ion and is almost immediately converted to nitrate, so that little nitrite is normally found in the environment. Under reducing conditions nitrate is converted primarily to nitrogen gas, a process known as **denitrification**. Organic matter will decay to ammonia under reducing conditions. Septic tank effluent, for example, normally has high ammonia and very little nitrate. If the receiving ground water is reducing, the nitrogen will stay in the ammonia form. If it is oxidizing, bacteria will convert the ammonia to nitrate (Feth 1966).

Nitrate contamination of ground water has been documented in a number of areas (e.g. Hill 1982; Flipse et al. 1984; and Silver and Fielden 1980). Hill studied the distribution

of nitrate in ground water from a shallow unconsolidated sand aquifer. It was found that the ground water beneath areas of forest or permanent pasture has less than 1.0 mg/L of nitrate as nitrogen. The ground water beneath heavily fertilized potato fields typically contained in excess of 10 mg/L nitrate as nitrogen. Gray and Morgan-Jones (1980) found that the nitrate content of ground water in a study area increased over the past 40 yr and that the use of fertilizers in this catchment area also increased over the same time period.

Nitrogen occurs as two isotopes, ^{14}N and ^{15}N . Of the two, ^{14}N is by far the most abundant in the atmosphere. The relative abundance of ^{15}N —that is, the $^{15}\text{N}/^{14}\text{N}$ ratio—in nitrate may be used to distinguish nitrate that comes from animal and human waste from nitrate that comes from mineral fertilizers (Flipse et al. 1984).

The $^{15}\text{N}/^{14}\text{N}$ ratio is usually expressed as a $\delta^{15}\text{N}$ value, which is defined as

$$\delta^{15}\text{N} (\text{‰}) = \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{standard}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} \times 1000$$

where ‰ stands for parts per thousand.

If the $\delta^{15}\text{N}$ is positive, then the nitrate of the sample has been enriched in ^{15}N with respect to the standard. For nitrogen, the standard is the atmospheric composition. Nitrate from animal and human waste typically has a $\delta^{15}\text{N}$ in excess of +10‰.

Flipse and Bonner (1985) found that mineral fertilizers used on Long Island had $\delta^{15}\text{N}$ values that averaged 0.2‰ at one site and -5.9‰ at another. However, the $\delta^{15}\text{N}$ of the ground water beneath the sites that had been fertilized was about +6‰. This increase in $\delta^{15}\text{N}$ from the mineral fertilizer was attributed to fractionation that occurred during infiltration of the nitrogen. However, the resulting $\delta^{15}\text{N}$ was still clearly lower than that expected from animal and human waste.

6.7.5 Arsenic

Arsenic can occur in valance states of +5, +3, +1, 0 and -3. However, the important states of dissolved arsenic in water are the arsenate $\text{H}_n\text{AsO}_4^{3-n}$, with a valance state of +5, and the arsenite $\text{H}_n\text{AsO}_3^{2-n}$, with a valance state of +3. An Eh-pH diagram for arsenic that shows the fields of stability for the arsenates and arsenites is given in Figure 6.9. Dissolved arsenic species can be absorbed by ferric hydroxides. Arsenic (+5) is more strongly sorbed than arsenic (+3). Ferric hydroxides are stable over a wide Eh-pH range, so this fact limits the mobility of arsenic. However, conditions that reduce Fe^{3+} to Fe^{2+} and As^{5+} to As^{3+} increase the mobility of arsenic in the environment, because the precipitated ferric hydroxides become soluble ferrous hydroxides (Matisoff, et al. 1982). In an oxidizing environment with a pH above 4.09, we will find colloidal ferric iron hydroxides, which will sorb arsenic and would thus expect to have little arsenic in solution. Under strongly reducing conditions, if both iron and hydrogen sulfide are present, arsenic sulfide coprecipitates with iron sulfide. Mildly reducing conditions that lack hydrogen sulfide present conditions under which one would expect to find the most mobile arsenic, as iron would be in the soluble ferrous state and arsenic would be in the arsenite form (Hounslow 1980).

Arsenic has been released to the environment through the burning of coal and the smelting of ores. In the past it was used in the formulation of insecticides and